UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2006/2007
Peperiksaan Semester Pertama
Sidang Akademik 2006/2007

Oktober/November 2006

EBP 202/3 - Polymer Structure
EBP 202/3 - Struktur Polimer

Time : 3 hours
Masa : 3 jam

Please ensure that this paper consists of FOURTEEN printed pages before you proceed with the examination.

This paper contains SEVEN questions.

Answer any FIVE questions. If a candidate answers more than five questions, only the first five answers will be examined and awarded marks.

Answer to any question must start on a new page.

All questions could be answered in Bahasa Malaysia or English.

Sila pastikan bahawa kertas peperiksaan ini mengandungi EMPAT BELAS muka surat yang bercetak sebelum anda memulakan peperiksaan.

Kertas soalan ini mengandungi TUJUH soalan.

Jawab LIMA soalan. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Mulakan jawapan anda untuk setiap soalan pada muka surat yang baru.

Semua soalan boleh dijawab samada dalam Bahasa Malaysia atau Bahasa Inggeris.

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1. [a] A sample of poly(vinyl chloride) is composed according to the following distribution

weight fraction, w_i	0.05	0.23	0.30	0.25	0.13	0.04
mean mol. wt., $M_i \times 10^{-3}$	7	11	16	23	31	39

Compute number-average molar mass, weight-average molar mass and polydispersity index.

(50 marks)

[b] Draw the following configuration of poly(styrene)

(i) isotactic

(ii) syndiotactic

(iii) atactic

(15 marks)

[c] Draw the possible conformation of poly(isobutylene) by using Newman projection.

(15 marks)

[d] (i) Differentiate between thermoplastic and thermoset.

(10 marks)

(ii) Give two examples and their chemical structure for thermoplastic.

(5 marks)

(iii) Give two examples and their chemical structure for thermoset.

(5 marks)

1. [a] *Satu sampel poli(vinil klorida) mempunyai taburan seperti berikut:*

pecahan berat, w_i	*0.05*	*0.23*	*0.30*	*0.25*	*0.13*	*0.04*
berat molekul purata, $M_i \times 10^{-3}$	*7*	*11*	*16*	*23*	*31*	*39*

Hitungkan jisim molar purata-nombor, jisim molar purata-berat dan indeks polidispersiti.

(50 markah)

[b] *Lukiskan konfigurasi bagi polistirena seperti yang berikut:*

(i) *isotaktik*

(ii) *sindiotaktik*

(iii) *ataktik*

(15 markah)

[c] *Lukiskan konformasi bagi poli(isobutilena) yang berkemungkinan dengan menggunakan unjuran Newman.*

(15 markah)

[d] *(i)* *Bezakan antara termoplastik dengan termoset.*

(10 markah)

(ii) *Berikan DUA contoh dan struktur kimia bagi termoplastik.*

(5 markah)

(iii) *Berikan DUA contoh dan struktur kimia bagi termoset*

(5 markah)

2. [a] The relationship of melting point with lamella thickness of polymer crystal can be given as;

$$T_m = T_m^o\left(1-\frac{2\gamma_e}{L\Delta H_v}\right)$$

State all terms available in the above equation.

(10 marks)

[b] Explain factors that influence the lamella thickness of a polymer crystal.

(30 marks)

[c] Show that for three dimensional spherulite growth, equation of crystallisation kinetics can be expressed as;

$$\frac{W_L}{W_o} = 1-\frac{\pi}{3}\left(\frac{\rho_s}{\rho_L}\right)N\,G^3\,t^4$$

Clearly state assumptions that are made and what is the significance of the value of 4 in the t^4 term.

(60 marks)

2. [a] *Hubungkait di antara takat lebur dengan ketebalan lamela hablur polimer diberikan sebagai;*

$$T_m = T_m^o\left(1-\frac{2\gamma_e}{L\Delta H_v}\right)$$

Nyatakan semua ungkapan yang terdapat dalam persamaan di atas.

(10 markah)

[b] *Terangkan faktor-faktor yang mempengaruhi ketebalan lamela hablur polimer.*

(30 markah)

[c] *Tunjukkan bahawa untuk pertumbuhan sferulit tiga dimensi, persamaan kinetik penghabluran dapat diberikan sebagai;*

$$\frac{W_L}{W_o}=1-\frac{\pi}{3}\left(\frac{\rho_s}{\rho_L}\right)N\,G^3\,t^4$$

Nyatakan dengan jelas anggapan-anggapan yang dibuat dan apakah signifikasi nilai 4 dalam ungkapan t^4.

(60 markah)

3. [a] A linear polyethylene has a molecular weight of 2.8×10^5. Given that the bond length of C-C and bond angle is 0.154 nm and 109.5^o respectively. Calculate the following:

(i) end-to-end distance in the extended state

(ii) contour length

(iii) RMS end-to-end distance

(50 marks)

[b] Write short notes on the following subject:

(i) freely-jointed chain model

(10 marks)

(ii) valence angle model

(10 marks)

(iii) RMS end-to-end distance

(10 marks)

(iv) RMS radius of gyration

(10 marks)

(v) long range steric restriction

(10 marks)

3. [a] *Satu polietilena linear mempunyai berat molekul 2.8 x 10^5. Diberikan panjang ikatan C-C dan sudut ikatan ialah 0.154 nm dan 109.5° masing-masing. Hitungkan*

(i) jarak hujung-ke-hujung dalam keadaan diperpanjang

(ii) panjang kontur

(iii) punca purata kuasa jarak hujung-ke-hujung

(50 markah)

[b] *Tuliskan nota ringkas bagi subjek berikut:*

(i) model rantai bersambung bebas

(10 markah)

(ii) model sudut valensi

(10 markah)

(iii) punca purata kuasa jarak hujung-ke-hujung

(10 markah)

(iv) punca purata kuasa jejari legaran

(10 markah)

(v) saling tindakan julat jauh

(10 markah)

4. [a] Flat film X-ray diffraction patterns obtained using CuKα beam (Ni filter) for an isotropic polypropylene yielded 2 sharp rings with each having radius of 12.6 and 19.5 mm respectively. With the assumption that molecular chain arrangement of polypropylene is monoclinic.

Given,

Specimen distance from film	= 50 mm
X-ray wavelength	= 0.154 nm

Polypropylene formed monoclinic with unit cell dimension and d_{hkl} respectively given as;

a = 0.666 nm	b = 2.78 nm	c = 0.650 nm
$\alpha = \gamma = 90^\circ \neq \beta$	$\beta = 99.6^\circ$	

$$d_{hkl} = \left[\frac{\left(h^2/a^2\right) + \left(l^2/c^2\right) - \left(2hl/ac\right)\cos\beta}{\sin^2\beta} + \frac{k^2}{b^2} \right]^{-1/2}$$

(i) Calculate the spacing of molecule planes distance, d, that produce the diffraction patterns.

(ii) Show that the diffraction rings were produced by by these planes (1 1 0) and (1 1 1).

(iii) If the polyethylene sample is subjected to extension, what kind of diffraction pattern would you expect?

(60 marks)

[b] Describe the use of optical microscope in the studies of polymer crystallisation.

(40 marks)

4. [a] *Pola pembelauan sinar-X filem rata untuk suatu kepingan polipropilena isotropik dengan menggunakan pancaran CuK_α (Penuras Ni) memberikan dua gelang yang mempunyai keamatan yang kuat dan jejari gelang tersebut berukuran 12.6 mm dan 19.5 mm. Dengan menganggap penyusunan rantai molekul polipropilena sebagai monoklinik,*

Diberi:

Jarak di antara spesimen dengan filem $= 50\ mm$
Jarak gelombang sinar-X $= 0.154\ nm$

Polipropilena membentuk hablur monoklinik dengan dimensi sel unit dan d_{hkl} *masing-masing sebagai;*

$a = 0.666\ nm \qquad b = 2.78\ nm \qquad c = 0.650\ nm$

$\alpha = \gamma = 90^o \neq \beta \qquad \beta = 99.6^o$

$$d_{hkl} = \left[\frac{\left(h^2/a^2\right) + \left(l^2/c^2\right) - \left(2hl/ac\right)\cos\beta}{\sin^2\beta} + \frac{k^2}{b^2} \right]^{-1/2}$$

(i) *hitungkan jarak ruangan antara satah yang menghasilkan pembelauan tersebut.*

(ii) *Tunjukkan bahawa gelang pembelauan tersebut adalah dihasilkan oleh satah (1 1 0) dn (1 1 1).*

(iii) *Sekiranya sampel polipropilena di atas dikenakan proses penarikan, apakah yang anda jangkakan tentang pola pembelauan sampel tersebut.*

(60 markah)

[b] *Terangkan penggunaan mikroskop optik dalam kajian penghabluran polimer.*

(40 markah)

5. [a] Explain for the differences in glass transition temperatures for the following pairs of isomeric polymers having similar chemical structures:

(i) poly(ethylene oxide) and poly(vinyl alcohol)

(10 marks)

(ii) poly(ethyl acrylate) and poly(methyl methacrylate)

(10 marks)

[b] Poly(vinyl alcohol) has T_g approximately 85°C. Proposed three alternatives to reduce the T_g of poly(vinyl alcohol) to 75°C.

(30 marks)

[c] Write short notes on the following subject:

(i) the WLF equation

(10 marks)

(ii) free volume theory

(10 marks)

(iii) polydispersity index

(10 marks)

(iv) glass transition temperature

(10 marks)

(v) random coil conformation

(10 marks)

5. [a] *Jelaskan perbezaan suhu peralihan kaca bagi pasangan polimer isomerik yang mempunyai struktur kimia yang agak sama seperti berikut:*

(i) *poli(etilena oksida) dan poli(vinil alkohol)*

(10 markah)

(ii) *poli(etil akrilat) dan poli(metil metakrilat)*

(10 markah)

[b] *Poli(vinil alkohol) mempunyai T_g menghampiri 85°C. Cadangkan TIGA cara untuk mengurangkan T_g bagi poli(vinil alkohol) ke 75°C.*

(30 markah)

[c] *Tuliskan nota ringkas bagi subjek berikut:*

(i) *persamaan WLF*

(10 markah)

(ii) *teori isipadu bebas*

(10 markah)

(iii) *indeks polidispersiti*

(10 markah)

(iv) *suhu peralihan kaca*

(10 markah)

(v) *konformasi gegelung rawak*

(10 markah)

6. [a] Describe five regions of viscoelastic for linear polystyrene and epoxy. Answer should be supported with suitable graph.

(50 marks)

[b] When Differential Scanning Calorimetry tests were conducted on two samples of polybutylene terephthalate (PBT), these results were obtained. PBT virgin sample (pellet) weighing 14.200 mg gave a melting enthalpy, ΔH_m, of 0.3005 Joule whereas another PBT sample (weighing 13.600 mg), which has gone through an injection moulding process recorded a melting enthalpy, ΔH_m, of 0.3599 Joule.

With the knowledge of melting enthalpy of a 100% PBT crsytal, ΔH^o_m is 140 Joule/g, calculate the degree of crystallinity of both PBT samples. Why there is a difference of melting enthalpy between these samples?

(50 marks)

6. [a] Huraikan lima kawasan kelakuan likat-kenyal bagi polistirena linear dan epoksi. Jawapan perlu disokong dengan graf yang bersesuaian.

(50 markah)

[b] Apabila suatu ujian Kalorimetri Penskanan Pembezaan dijalankan ke atas dua sampel polibutilena tereftalat (PBT), keputusan berikut diperolehi. Sampel asal (pelet) PBT seberat 14.200 mg memberikan entalpi peleburan, ΔH_m = 0.3005 Joule manakala sampel PBT yang telah mengalami proses pengacuanan suntikan (seberat 13.600 mg) merekodkan entalpi peleburan ΔH_m = 0.3599 Joule.

Berbantukan maklumat entalpi peleburan untuk 100% hablur PBT, (ΔH^o_m = 140 Joule/g), kirakan darjah keterhabluran bagi kedua-dua sampel PBT tersebut. Mengapakah terdapat perbezaan entalpi peleburan di antara sampel-sampel tersebut?

(50 markah)

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7. [a] With the assistance of data given below, determine degree of crystallinty of low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE).

Given;

Density of polyethylene crystal	= 1000 kg/m^3
Specific volume of amorphous polyethylene	= 1.156 x 10^{-3} m^3/kg
Density of LDPE	= 920 kg/m^3
Density of LLDPE	= 940 kg/m^3
Density of HDPE	= 960 kg/m^3

(30 marks)

[b] Explain why there are differences in degree of crystallinity for LDPE, LLDPE and HDPE although they came from the same polymer group.

(40 marks)

[c] Describe another method that can be used to determine the degree of crystallinity of a polymer.

(30 marks)

7. [a] *Berpandukan data yang diberikan di bawah, tentukan nilai darjah keterhabluran bagi polietilena ketumpatan rendah (LDPE), polietilena linear ketumpatan rendah (LLDPE) dan polietilena ketumpatan tinggi (HDPE).*

Diberi:

Ketumpatan polietilena berhablur	$= 1000\ kg/m^3$
Isipadu spesifik polietilena amorfus	$= 1.156 \times 10^{-3}\ m^3/kg$
Ketumpatan LDPE	$= 920\ kg/m^3$
Ketumpatan LLDPE	$= 940\ kg/m^3$
Ketumpatan HDPE	$= 960\ kg/m^3$

(30 markah)

[b] *Terangkan mengapa wujud perbezaan darjah keterhabluran bagi LDPE, LLDPE dan HDPE walaupun ketiga-tiga polimer tersebut berasal daripada kumpulan polimer yang sama.*

(40 markah)

[c] *Terangkan kaedah lain yang boleh digunakan untuk menentukan darjah keterhabluran suatu polimer.*

(30 markah)

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